

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE October 10, 1996	3. REPORT TYPE AND DATES COVERED Final Report 9/1/93 - 8/31/96
4. TITLE AND SUBTITLE Environmental Effects on High Energy Density Materials			5. FUNDING NUMBERS 61102F2303B3
6. AUTHOR(S) Henry F. Schaefer III			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Georgia Univ Research Foundation Inc Boyd Grad Studies Res Cntr Athens, GA 30602			8. PERFORMING ORGANIZATION AFOSR-TR-96 OSII
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NEL Building 410, Bolling AFB DC 20332-6448 Dr. Michael R. Berman			10. SPONSORING/MONITORING AGENCY REPORT NUMBER 1 F49620-93-J-0529
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) The <u>object</u> of this research is to characterize, using <u>ab initio</u> quantum mechanical methods, the stabilizing or destabilizing effects of hydrogen and/or oxygen matrices on proposed high energy density molecular (HEDM) systems. In addition, the unimolecular fragmentation reactions of large HEDM species such as N ₂ O will be studied via density functional methods. 19961028 006			
14. SUBJECT TERMS <u>Ab initio</u> , computational chemistry, quantum chemistry, theoretical chemistry, propellants.			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

DTIC QUALITY INSPECTED 1

Final Technical Report
Air Force Office of Scientific Research
Grant F49620-93-1-0529

"Environmental Effects on High Energy Density Materials"

Principal Investigator: Henry F. Schaefer III
Center for Computational Quantum Chemistry
University of Georgia

I. Summary

The development of efficient and safe conventional (i.e., nonnuclear) propellants and/or fuels is a goal of obvious technological significance. A desirable quality of such a propellant is clearly a high ratio of energy release to mass. The present hypothesis rests on a simple, but previously unrecognized, analogy between oxygen and sulfur. Preliminary studies showed that the oxygen ring systems are sufficiently promising to warrant the detailed, high-level theoretical research reported here.

Our idea begins with the observation that elemental sulfur exists as sulfur rings, S_n . The essence of our proposal is to make an analogy between sulfur rings and oxygen rings. Given the remarkable stability of sulfur rings, should it not be possible to prepare oxygen rings? Oxygen lies directly above sulfur in the Periodic Table, and the analogy is an appealing one.

Work completed includes our study of the prospective HEDM material $C_2H_2Li_2$. This molecule has been of sustained intellectual interest since 1976 when Paul Schleyer and John Pople suggested that the lowest triplet state of 1,1 -dithioethylene might allow nearly free rotation about the supposed classical $C=C$ "double bond". In 1985 Manceron

and Andrews intercepted dilithioethylene via matrix isolation infrared spectroscopy in the laboratory. Moreover, in 1987 Maercker, Graule, and Demuth used mercury precursors to characterize *cis* and *trans* 1,2-dilithioethylene as more conventional reaction products. So this species is by no means simply a figment of the theorist's imagination.

The work I describe was published in the *Journal of the American Chemical Society*, having been carried out jointly with the Proctor and Gamble Company. The bulk of the research was carried out by my graduate student Evan Bolton, supported by the AASERT program.

The potential energy surface (PES) for the singlet 1,2-dilithioethene and acetylenic $C_2H_2Li_2$ isomers was carefully surveyed using high level quantum mechanical methods. Three previously undiscovered minima (including, remarkably, the global minimum) were located: a planar monobridged *trans* 1,2 dilithioethene and two acetylenic structures. A total of seven minima and ten transition states for interconversion of minima were investigated, while seven transition states are located for the first time. Vibrational frequencies were evaluated for all structures through the coupled-cluster method including all single and double excitation with a double- ζ plus polarization basis set. A remarkable isomer, the C_s complex between lithioacetylene and LiH, is the global minimum on the $C_2H_2Li_2$ PES. This structure was 34 kcal/mol more stable than the two lowest lying singlet 1,2-dilithioethene structures, a *trans* planar C_{2h} form with acute CCLi angles and a *cis* doubly bridged C_{2v} structure. The other singlet 1,2-dilithioethene minima, *cis* planar monobridged C_s , *cis* planar dibridged C_{2v} , and *trans* planar monobridged C_s , are 4.3, 8.4, and 19.4 kcal/mol higher lying, respectively. The carbon-lithium bonding is ionic in character in all these species.

Another important study has been carried out by graduate student John Galbraith and published recently in the *Journal of the American Chemical Society*. Motivated by the recent isolation and spectroscopic characterization of nitrosyl azide (N_4O), we have undertaken an *ab initio* investigation of the originally reported structure as well as various structural isomers on the potential energy hypersurface. Geometries and harmonic vibrational frequencies have been predicted for the *trans*-chain isomer, along with the 6 π -electron potentially aromatic ring structure, with various levels of theory up through the triple- ζ plus double polarization single and double excitation coupled cluster (TZ2P CCSD) method and the multi-reference configuration interaction method (MRCISD). In addition, estimates are made for extension to higher levels of theory, arriving at final structural predictions for the *trans*-chain and ring isomers. Energy relationships, bond lengths, vibrational frequencies, Mulliken bond indices, and molecular orbital arguments are used to elucidate the nitrogen oxide bonding. While the ring isomer is predicted to be the most stable structure on the hypersurface, the barrier to dissociation is most likely between 1 and 2 kcal mol⁻¹ (including zero point vibrational energy [ZPVE] the existence of any barrier becomes questionable), making isolation theoretically possible but experimentally difficult. This small barrier also detracts from the attractiveness of the N_4O ring structure as a high energy-density material. The *trans*-chain isomer, however, lies in an energy valley with higher sides, consistent with its experimental observation.

II. Publications Supported by F49620-93-J-0529

1. E. E. Bolton, H. F. Schaefer, W. D. Laidig, and P. R. Schleyer, "Singlet $\text{C}_2\text{H}_2\text{Li}_2$: Acetylenic and 1, 2 - Dilithioethene Isomers. A Remarkably Congested Potential Energy Hypersurface for a Simple Organometallic System", *J. Amer. Chem. Soc.*, **116**, 9602 (1994).
2. M. L. Leininger, C. D. Sherrill, and H. F. Schaefer, " N_8 : A Structure Analogous to Pentalene and Other High Energy Density Minima," *J. Phys. Chem.* **99**, 2324 (1995).

3. P. R. Schreiner, H. F. Schaefer, and P. R. Schleyer "Can AlH_5 Exist?", *J. Chem. Phys.* **103**, 5565 (1995).
4. E. E. Bolton, W. D. Laidig, P. R. Schleyer, and H. F. Schaefer, "Does Singlet 1,1 Dilithioethene Really Prefer a Perpendicular Structure?" *J. Phys. Chem.* **99**, 17551 (1995).
5. J. M. Galbraith and H. F. Schaefer, "The Nitrosyl Azide (N_4O) Potential Energy Hypersurface: A High Energy-Density Boom or Bust?", *J. Amer. Chem. Soc.* **118**, 4860 (1996).
6. J. C. Stephens, E. E. Bolton, and H. F. Schaefer, "Quantum Mechanical Vibrational Frequencies and Matrix Isolation Assignments for Al_2H_2 ", *J. Chem. Phys.* submitted.
7. A. Tian, F. Ding, L. Zhang, Y. Xie, and H. F. Schaefer, "New Isomers of N_8 without Double Bonds", *J. Phys. Chem.* submitted.

III. List of Participating Professionals

A. Senior Research Personnel:

Professor Henry F. Schaefer III

B. Junior Research Personnel:

Mr. Evan E. Bolton

Mr. Matthew L. Leininger

Mr. John M. Galbraith

Mr. C. David Sherrill

Mr. Jeffrey C. Stephens